INTERPRETATION OF GAS CHROMATOGRAPHIC SPECTRA IN ROUTINE ANALYSIS OF GASOLINE EXHAUST HYDROCARBONS

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INTRODUCTION

In studies of atmospheric pollution from automobile emissions a practical meth is required to routinely analyze the emission samples for hydrocarbon components, and that method must be sensitive and capable of discriminating hydrocarbons of different molecular size and different photochemical reactivity.[1/] To meet this ne the Bureau is developing a gas chromatographic (GLC) method as a part of its studie of environmental contamination from motor gasoline combustion.

Earlier work resulted in a chromatographic method with adequate sensitivity a acceptably short analysis time[2/]. Interpretation of the chromatographic spectra w questionable, however, because it was based on a single set of peak-identity assig ments obtained from only a few exhaust samples. For more accuracy, spectra inter- pretation should be based on peak-identity assignments obtained separately for eac exhaust sample -- a tedious and time-consuming practice. When numerous exhaust samples must be analyzed daily, a common requirement, a rapid and accurate method chromatographic spectra interpretation, is needed. The study undertaken to develo such a method and the results of that study are described in this report.

EXPERIMENTAL PROCEDURES

The objective of this study was to explore the use of chromatographic-column retention times for identifying component peaks. With adequate retention time repeatability[2/], the success of this peak-identification method depends only on t degree to which the composition of the material represented by each peak is cons Preliminary evidence suggested that composition within each of most of the peaks a chromatogram of exhaust emissions is indeed constant, at least among exhaust sa obtained from different engines using the same fuel. Additional data were needed confirm or refute that evidence.

The ideal experimental procedure would have called for tests to determine pea identities in chromatograms of exhaust samples obtained from a variety of engines and fuels. To simplify the procedure, one engine was operated with varied air-fu ratios and ignition-timing conditions because, in our opinion, differences in the composition of combustion products from different engines, using the same fuel, result primarily from differences in air-fuel ratio and ignition timing. For veri fication, data obtained from tests with one fuel and four engines operated at two ambient temperatures were included in this study.

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A 1968 Valiant, equipped with a 6-cylinder, 225-CID engine, was operated following the 7-mode California cycle on a chassis dynamometer under four sets of engine conditions: Rich, with vacuum spark advance (VSA); rich, without VSA; lean, with VSA; and lean, without VSA. Compositions of the three experimental fuels were as follows:

Fuel No.	Component level, volume %		
	Saturates	Olefins	Aromatics
1	66.0	15.1	18.9
2	60.7	10.2	29.1
3	53.1	1.9	45.0

Four automobiles, a 1968 Delta 88 (455 CID), a 1968 Fury I (318 CID), a 1968 Impala (307 CID), and a 1968 Galaxie (302 CID), were operated identically as described for the Valiant automobile. All four cars were operated with the fuel No. 4, at ambient temperatures of 70° and 95° F. The composition of fuel No. 4 was: Saturates, 41.8%; olefins, 12.4%; aromatics, 45.8%.

All fuel and exhaust samples were collected and analyzed by the routine methods of this laboratory[2]. Peaks in the resultant chromatographic spectra were identified by a subtractive column technique[3], and from retention time and component stability data. Subtractive agents used were mercuric sulfate, sensitive to unsaturated aliphatics, and palladium sulfate, sensitive to aromatics. Exhaust was analyzed chromatographically before and after passing through the subtractive columns. Thus, each peak in the chromatogram from the untreated exhaust was identified as a hydrocarbon type (paraffin, aliphatic unsaturate, aromatic) or, if a mixture of hydrocarbons, the composition of that mixture was described. Also, exhaust samples were allowed to stand in the dark and under solar irradiation, and component losses were measured. From these component-loss data, peaks representing components that are thermally and photochemically reactive were identified.

Because the identification of peaks was based mainly on the subtractive column data and because the performance of the subtractive agents was questionable, synthetic mixtures of paraffins, olefins, and aromatics of varying structure and molecular size were prepared and used to evaluate the performance of the subtractive columns.

RESULTS AND DISCUSSION

Results from measurements of efficiency of the subtractive columns showed two anomalies in the function of the mercuric sulfate column. First, contrary to expectations, certain olefins were not removed quantitatively by the column. Second, new peaks appeared in the chromatograms of column-treated samples. Further investigation of these new peaks by mass spectrometry revealed that they represented 3-methyl-2-butanone and 3-methyl-2-pentanone, formed from reaction of the subtractive agent with 2-methyl-2-butene and 3-methyl-*trans*-2-pentene, respectively. Mercury sulfate, therefore, is inadequate as a subtractive agent for certain hydrocarbons, but current data do not permit linking this inadequacy to a specific class or classes of exhaust components. The problem was considered in subsequent work in peak identification, and data were analyzed carefully to obtain peak identities least affected by the deficiencies of the subtractive column.

Results from the peak-identification study generally verified the earlier observation that composition of material represented by each peak in exhaust chromatograms is nearly constant among all the chromatograms of exhaust from different engines but the same fuel. Results were as follows:

In the tests with three fuels and one engine operated under varied conditions, each exhaust chromatogram contained about 165 peaks of which 135 to 145 represented either individual components or mixtures of components of similar type. The remain 20 to 30 peaks represented mixtures of different type components, such as paraffins with olefins or with aromatics. When the chromatographed exhaust samples originate from different fuels, the composition of the material represented by each peak vari significantly from chromatogram to chromatogram. When the exhaust samples were obtained under varied engine conditions but with the same fuel, variation in within peak composition was much smaller and comparable to the variation caused by experimental error. The magnitude of this variation in within-peak composition is best evaluated from its effect upon the chromatographic analysis, as illustrated next.

In emission studies, chromatographic analyses are commonly used to compute the reactivity or pollution potential of exhaust hydrocarbon emissions. This computati follows Jackson's equation[4/]

$$R = \Sigma X_i \, r_i$$

where R designates reactivity of the exhaust hydrocarbon mixture, and X_i and r_i are mole fractions and specific reactivities, respectively, of ith component. By use of mole fraction values for a typical exhaust and published values for specific rate-of-NO_2-formation reactivities[4/], the variation in within-peak composition observed in these tests was calculated to cause maximum variation in exhaust reactivity value equivalent to ± 2.3%, ± 1.8%, and ± 1.7% for fuels 1, 2, and 3, respectively.

Similar results were obtained from the tests using four engines and fuel No. 4 Variation in within-peak composition among the exhaust chromatograms was equivalent to a ± 2.0% variation in exhaust reactivity value.

Part of any observed variation in within-peak composition is caused by experimental error. Thus, for any two chromatograms from replicate tests, the range of within-peak compositions was as much as about one-half of that observed among chromograms from all tests. Therefore, true variation in within-peak composition should affect calculated reactivity values by no more than about ± 1%, which is considered unimportant.

These results indicate that in chromatograms of exhaust from different engines but the same fuel, each peak represents nearly the same component or component mixture. This simplifies spectra interpretation because exhaust peaks must be identified only once for each parent fuel. These peak identities, consequently, can be used to interpret chromatographic spectra of all exhaust samples from that fuel. This method of interpreting chromatographic spectra is now used routinely by the Bureau of Mines[2/].

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